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DETERMINATION OF PARAMETERS OF A NEW METHOD FOR PREDICTING ALLOY PROPERTIES

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Abstract

Recently, a semiempirical method for alloys based on equivalent crystal theory was introduced (Phys. Rev. B45,943(1992)). The method successfully predicts the concentration dependence of the heat of formation and lattice parameter of binary alloys. In this report, a study of the parameters of the method is presented, along with new results for γ Fe-Pd and γFe-Ni alloys.

Recently, a new method for calculating alloy properties was introduced by Bozzolo, Ferrante and Smith (BFS)[1]. The method is based on the ideas of equivalent crystal theory (ECT) for defect formation energies in elemental solids[2] and uses only pure metal and two alloy properties as input data. In our previous work, we applied the method to the study of the heat of formation as well as the concentration dependence of the lattice parameter of several fcc binary alloys[1,3]. More recent applications of BFS deal with the study of the energetics of bcc alloys[4] and theoretical modelling of the atomic force microscope for bimetallic tip-sample interactions[5]. Also, as a consequence of the ideas underlying the foundation of BFS, we were able to derive a new set of sum rules which allow for the direct calculation of bulk alloy properties from pure component properties[6].

The simplicity of the method relies on the basic assumption that the energy of each non-equivalent atom is described as a superposition of two separate contributions: a strain energy that deals with the structural changes and a chemical energy that takes into account the changes in chemical composition. The calculation of the first term, the strain energy, is a straightforward application of equivalent crystal theory for pure elements: it is computed as if the neighbors of a given atom were of the same atomic species. Thus, no information for the alloy is needed except for neighbor locations. The calculation of the chemical energy follows an ECT-like format with the introduction of two additional 'perturbative' parameters which mimick the interaction between atoms of different atomic species in the overlap region and account for the changes in the electron density due to the presence of the other atomic species[1]. For binary alloys A-B, two such parameters are needed, Δ_{AB} and Δ_{BA}, which are obtained from two experimental (or theoretical) alloy properties as input[1]. Our previous work[1,3-6] only cited the application of BFS to several problems in order to

verify its ability to predict properties of interest. We now give a more detailed discussion concerning the properties of Δ_{AB} and Δ_{BA} and provide a set of values for general use.

In our previous work[1,3-5], Δ_{AB} and Δ_{BA} were determined by requiring that the predicted heats of solution in the dilute limit reproduced the experimental values. These quantities were computed by making use of the cluster expansion method[7] which relates properties of ordered compounds to those of disordered. We used it to predict the heat of formation for disordered alloys. Although this scheme has been very successful in a large number of applications[8-10], there is still some uncertainty regarding the truncation criteria used in the expansion[11]. This arbitrariness results in fluctuations of the predicted values of Δ_{AB} and Δ_{BA}. In some cases, the choice of a basis set on which the expansion is based could lead to theoretical predictions that differ greatly from the experimental ones, even if the physical quantity used as input (i.e., the heat of solution) is accurately reproduced. We will give an example of this along with providing a set of parameters Δ_{AB} and Δ_{BA}, used in our previous work[1,3-5], and comment on the sensitivity of these parameters to the choice of truncation scheme used in the cluster expansion.

Table 1 displays the pure element parameters needed for computing the strain and chemical energy contributions[1,2] and Table 2 shows the parameters Δ_{AB} and Δ_{BA} for several fcc binary alloys of the elements listed in Table 1, obtained by using the tetrahedron approximation[8] (i.e., all the clusters contain only nearest-neighbors). In all cases we used the experimental heats of solution in the dilute limit as input, as this quantity is readily available for most alloys[12]. Previous applications of this nearest-neighbor model to total energy of bulk alloys can be found in the work of Connolly and Williams[8], Terakura et al[9] and Takizawa et al[10]. The ordered structures included in order to determine the many-body

potentials in the cluster expansion are the fcc $L1_0$ and $L1_2$ structures. It was found that this basis set gives good results for all the alloys listed in Table 2. In tables 3 and 4 we display the corresponding parameters for bcc pure elements and binary alloys respectively.

To the fcc binary alloys discussed in Ref. 1 , we added two new cases: γFe-Pd and γFe-Ni. The qualitative and quantitative agreement are good in both cases. Fig. 1 shows the heat of formation as a function of composition for these two disordered alloys.

In table 5 we address the issue of stability of the parameters Δ with respect to the choice of basis set of ordered compounds in the cluster expansion for a Cr-V alloy[4]. The different choices are related to two possible ordered structures at 50 % composition ($B2$ and $B32$) and the corresponding pair multisite correlation functions (ξ_2 and ξ_3). We will denote the cases studied as follows: (i) $B32$-ξ_2:includes the $B32$ ordered structure and the ξ_2 correlation function (nearest-neighbor pair); (ii) $B32$-ξ_3; $B2$-ξ_2 and (iv) $B2 + B32$-$\xi_2 + \xi_3$ (see Ref. 4 for details). We note that the ambiguity in the values of such parameters is a consequence of the cluster expansion method and basis set chosen. Otherwise, we would expect to be able to define a unique set of parameters Δ for different alloys if no approximate schemes (for example, *ab initio* calculations) were involved in the theoretical determination of the property of choice. Figure 2 displays some results for the heat of formation of the Cr-V alloy (see Ref. 4 for a more detailed discussion). The several curves shown correspond to different choices of the basis set chosen, although the same experimental input is used in all cases. Obviously, the extreme difference in behavior of the heat of formation is purely a consequence of the basis set used and not of the formalism presented here. Actually, the parameters obtained for different basis sets are fairly stable: the parameters Δ play the role of perturbations on the ECT parameter α (see table 1 and 3), giving a net change in α of

Element	Cohesive Energy	Lattice Constant	p	l	α	λ
Al	3.34	4.05	4	0.336	2.105	0.944
Cu	3.50	3.615	6	0.272	2.935	0.765
Ag	2.96	4.086	8	0.269	3.337	0.756
Au	3.78	4.078	10	0.236	4.339	0.663
Ni	4.435	3.524	6	0.270	3.015	0.759
Ir	6.94	3.84	10	0.235	4.408	0.661
Pd	3.94	3.89	8	0.237	3.612	0.666
Pt	5.85	3.92	10	0.237	4.535	0.666
Fe	4.27	3.57	6	0.279	2.963	0.784

Table 1: Experimental input: Cohesive energy (in eV), lattice parameter (in A). ECT parameters: p, l (in A), α (in A^{-1}) and λ (in A) for several fcc elements.

the order of 0.01%. Thus in spite of the ability to obtain quantitatively accurate predictions in many cases it would be desirable to base the values of Δ on first-principles calculations.

A-B	Δ_{AB}	Δ_{BA}
Ag-Al	0.0475	-0.0499
Ag-Au	-0.0333	-0.0227
Ag-Cu	-0.0391	-0.0308
Ag-Pd	-0.0451	-0.0178
Al-Au	-0.0501	-0.0853
Al-Cu	-0.0526	-0.0626
Al-Ni	-0.0657	-0.0861
Au-Cu	-0.0513	-0.0604
Au-Ni	-0.0506	-0.0622
Au-Pd	-0.0460	-0.0345
Cu-Fe	0.0495	0.0638
Cu-Ni	-0.0163	0.0309
Cu-Pd	-0.0431	-0.0495
Cu-Pt	-0.0585	-0.0441
Fe-Ni	-0.0106	-0.0320
Fe-Pd	-0.0229	-0.0584
Ni-Pd	-0.0396	-0.0478
Ni-Pt	-0.0609	-0.0537

Table 2: Parameters Δ_{AB} and Δ_{BA} for several fcc binary alloys.

Element	Cohesive Energy	Lattice Constant	p	l	α	λ
W	8.66	3.16	10	0.274	4.232	0.770
Ta	8.10	3.30	10	0.325	3.905	0.914
Mo	6.82	3.15	8	0.262	3.420	0.736
Nb	7.57	3.30	8	0.341	3.243	0.958
V	5.31	3.03	6	0.305	2.726	0.857
Cr	4.10	2.88	6	0.254	2.889	0.714
Fe	4.29	2.86	6	0.277	3.124	0.770
Li	1.63	3.491	2	0.589	1.049	1.66
Na	1.113	4.225	4	0.578	1.359	1.62
K	0.934	5.225	6	0.694	1.528	1.95
Rb	0.852	5.585	8	0.651	1.937	1.83
Cs	0.804	6.045	10	0.757	2.115	2.13

Table 3: Experimental input: Cohesive energy (in eV), lattice parameter (in A). ECT parameters: p, l (in A), α (in A^{-1}) and λ (in A) for several bcc elements.

A-B	Δ_{AB}	Δ_{BA}
Cr-Fe	0.0465	0.0285
Cr-Mo	-0.02447	-0.0090
Cr-V	-0.0246	-0.0232
Fe-V	0.0998	-0.07168

Table 4: Parameters Δ_{AB} and Δ_{BA} for several bcc binary alloys.

Basis	Δ_{AB}	Δ_{BA}
i	-0.0242	-0.0228
ii	-0.0246	-0.0232
iii	-0.0232	-0.0222
iv	-0.0237	-0.0225

Table 5: Parameters Δ_{AB} and Δ_{BA} for different basis sets used in the cluster expansion (see Ref. 4) for Cr-V.

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